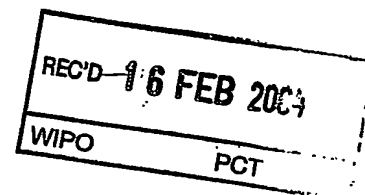




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Patentanmeldung Nr. Patent application No. Demande de brevet n°

03405448.6

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Ciba Specialty Chemicals Holding Inc.  
Klybeckstrasse 141  
4057 Basel  
SUISSE

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(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
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Process for incorporation of UV-luminescent compounds in polymeric materials

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**Process for Incorporation of UV-luminescent Compounds in Polymeric Materials**

The present invention relates to a process for the preparation of UV luminescent polymeric materials and their uses.

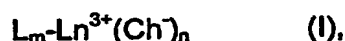
There is a need for furnishing textiles with covert effects, which may act as security markings, as special effects or as decorations that only become visible under UV irradiation.

It is therefore an object of the present invention to provide a dyeing composition comprising a substance which is invisible to the unaided eye but yields a strong luminescence under UV exposure and which composition can be used for all conventional dyeing applications of polymeric materials including textiles such as wool, silk, cellulosic materials, natural and synthetic fibres as well as for the mass dyeing of polymeric materials including those used in textile and plastic applications.

The invention relates to a process for the preparation of luminescent polymeric fibres characterised in that the fibres are treated with a composition comprising

- (a) one or more luminescent lanthanide chelates containing three or four organic anionic ligands having at least one UV absorbing group and
- (b) one or more solvents.

Preferably, component (a) is a compound of formula I



wherein Ln represents a lanthanide,

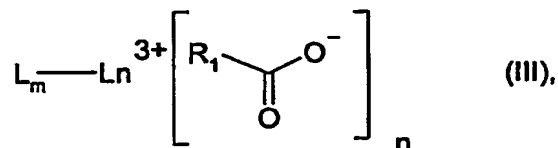
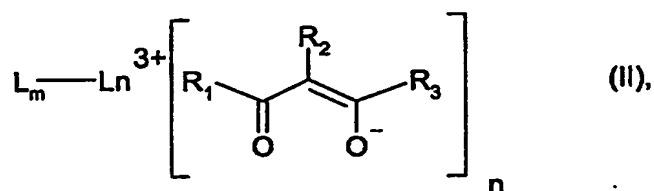
Ch<sup>-</sup> is a negatively charged ligand containing at least one UV absorbing double bond,

n denotes 3 or 4, m denotes a number from 0 to 4,

in case n is 3, m denotes a number from 0 to 4 and L is a neutral monodentate or

polydentate nitrogen-, oxygen- or sulfur-containing ligand or, in case n is 4, m denotes 1 and L is a single-charged cation.

More preferably, component (a) is a compound of formula II, III or IV



wherein Ln represents a lanthanide,

n denotes 3 or 4, m denotes a number from 0 to 4

in case n is 3, m denotes a number from 0 to 4 and L is a neutral monodentate or polydentate nitrogen-, oxygen- or sulfur-containing ligand or, in case n is 4, m denotes 1 and L is a single-charged cation,

R<sub>2</sub> is hydrogen or C<sub>1</sub>-C<sub>6</sub>alkyl, and

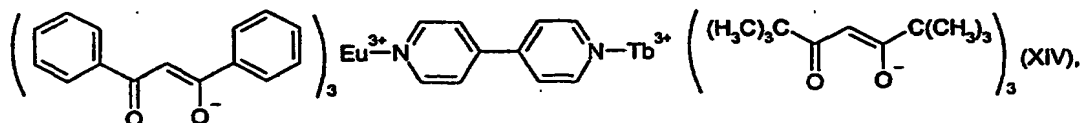
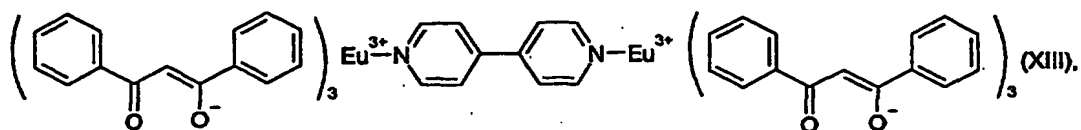
R<sub>1</sub> and R<sub>3</sub> are each independently of the other hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, CF<sub>3</sub>, C<sub>5</sub>-C<sub>24</sub>aryl or C<sub>4</sub>-C<sub>24</sub>heteroaryl.

The compounds of formula I, II, III or IV can basically contain any neutral monodentate or polydentate nitrogen-, oxygen- or sulfur-containing ligand such as, for example, unsubstituted or substituted pyridine, pyrazine, piperidine, quinoline, aniline, bipyridine, phenanthroline, terpyridine, imidazole, benzimidazole, bisimidazole, bisbenzimidazole, pyrimidine, bipyrimidine, naphthyridine, alkylamine, dialkylamine, trialkylamine, alkylene polyamine, dioxane, dimethylsulfoxide, dimethylformamide, phosphine-oxide derivative (trialkyl or triaryl), triazine, bistriazine, oxazole, bisoxazole, oxazoline, bisoxazoline and substituted derivatives thereof and all relevant (poly)N-oxide derivatives of above cited ligands.

Particularly preferred are compounds of formula I, II, III or IV wherein n denotes 3 and L is a nitrogen-containing ligand.

Since L can be a polychelating ligand, like for example 4,4'-bipyridyl, the compounds of formula I, II, III and IV include multimetallic chelates, such as for example the compounds of

formula XIII and XIV, containing two  $M^{III}-(\text{diketone})_3$  or  $M^{III}-(\text{carboxylate})_3$  units connected via a bidentate ligand:

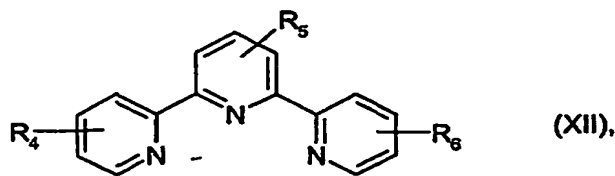
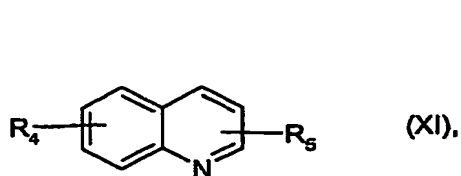
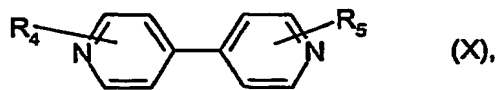
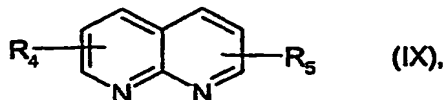
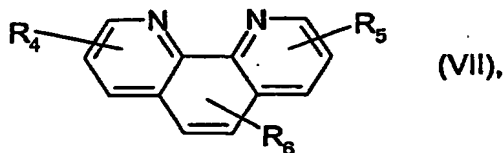
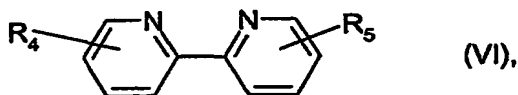
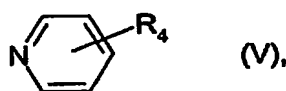


When n denotes 4, L as single-charged cation can be basically any metal cation (e.g.  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ), unsubstituted or substituted ammonium (e.g.  $\text{NH}_4^+$ , polyalkylammonium) or any protonated or alkylated monodentate or polydentate ligand as described above.

Preferred positively charged ligands are piperidinium, ammonium, alkylammonium, dialkylammonium and, in particular, trialkylammonium.

Triethylammonium is especially preferred.

Particularly preferred are compounds of formula I, II, III or IV wherein L is a compound of formulae V to XII



or a cation of the formula  $\text{H}-\text{N}^+(\text{R}_7)_3$ ,

wherein  $R_4$ ,  $R_5$  and  $R_6$  are each independently of the other hydrogen, halogen,  $C_1$ - $C_6$ alkyl,  $C_5$ - $C_{24}$ aryl,  $C_6$ - $C_{24}$ aralkyl,  $C_1$ - $C_6$ alkoxy, amino, dialkylamino or a cyclic amino group and  $R_7$  is hydrogen,  $C_1$ - $C_6$ alkyl,  $C_5$ - $C_{24}$ aryl,  $C_6$ - $C_{24}$ aralkyl or vinyl.

Alkyl groups as substituents  $R_1$  to  $R_7$  can be straight chain or branched. Examples which may be mentioned are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, Isobutyl, tert-butyl, n-pentyl, neopentyl, isopentyl, n-hexyl and isohexyl.

Alkoxy groups as substituents  $R_4$  to  $R_6$  can be, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy or tert-butoxy.

Examples of  $C_5$ - $C_{24}$ aryl groups are phenyl, tolyl, mesityl, isityl, diphenyl, naphthyl and anthryl. Phenyl is preferred.

Heteroaryl group preferably contain 4 or 5 C atoms and one or two heteroatoms selected from O, S and N. Examples are pyrrolyl, furanyl, thiophenyl, oxazolyl, thiazolyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolyl, purinyl or chinolyl.

Aralkyl groups as substituents  $R_4$  to  $R_7$  can be, for example, benzyl, 2-phenylethyl, tolylmethyl, mesitylmethyl and 4-chlorophenylmethyl.

Suitable dialkylamino groups are, for example, diethylamino, diisopropylamino, di-n-propylamino, N-methyl-N-ethylamino and, in particular, dimethylamino or pyrrolidino.

Suitable cyclic amino groups are pyrrolidino and piperidino.

Halogen atoms as substituents  $R_4$  to  $R_6$  are preferably fluorine, chlorine or bromine, but in particular chlorine.

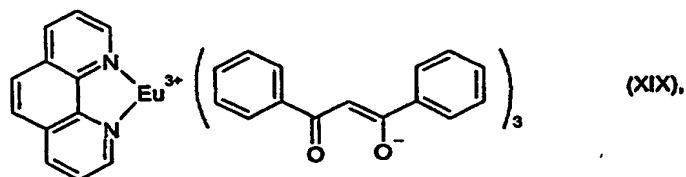
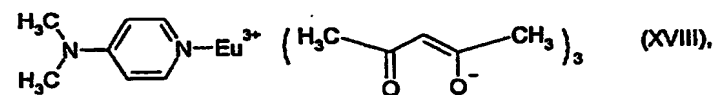
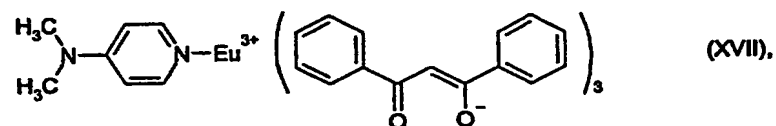
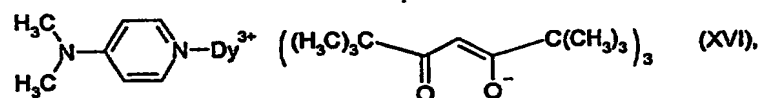
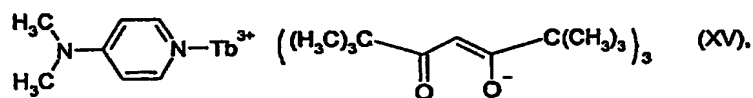
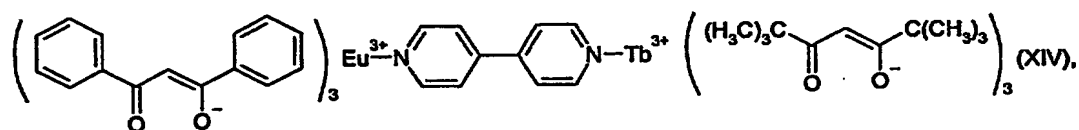
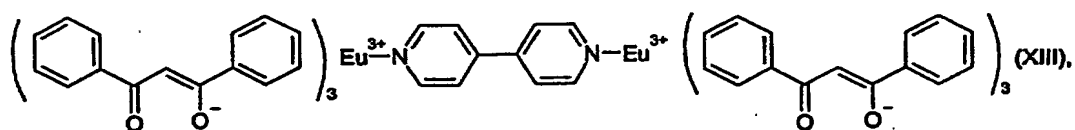
Preferred compositions according to the invention contain as component (a) a compound of formula II wherein L is a compound of formula V, VI, VII, VIII, IX, X, XI or XII wherein  $R_4$ ,  $R_5$  and  $R_6$  are hydrogen, methyl, amino, pyrrolidino or dimethylamino or L is a cation of the formula  $H-N^+(R_7)_3$  wherein  $R_7$  is  $C_1$ - $C_6$ alkyl.

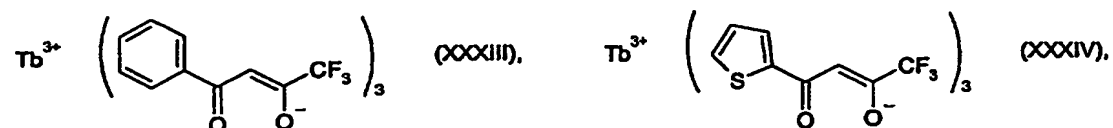
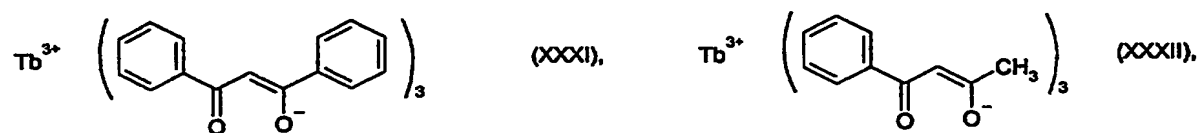
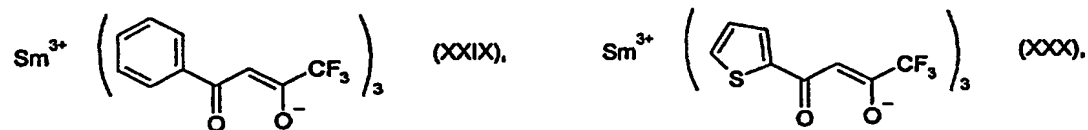
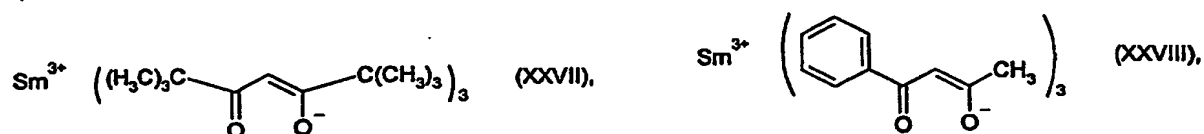
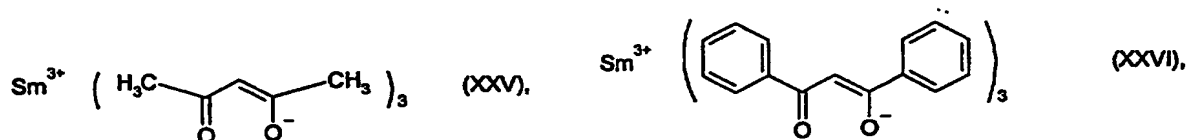
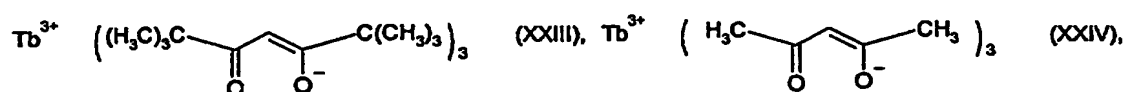
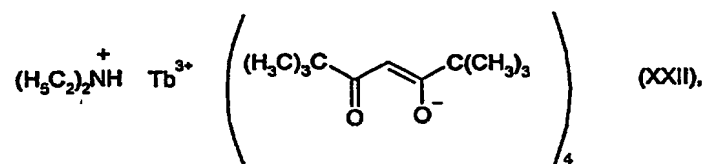
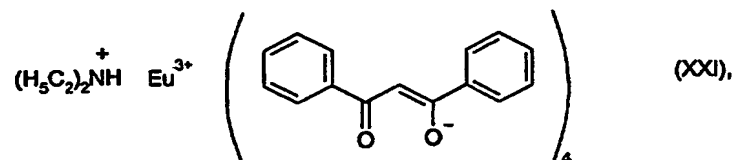
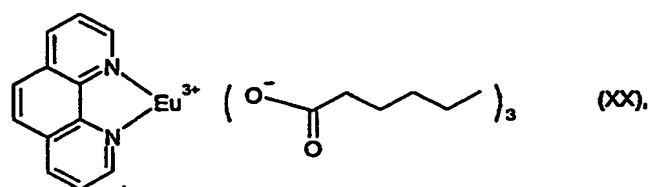
Preferred components (a) are compounds of formula I, II, III or IV wherein Ln is Eu, Tb, Dy, Sm or Nd.

Furthermore, compounds of formula II and III are preferred, wherein R<sub>1</sub> and R<sub>3</sub> are methyl, t-butyl, n-pentyl or phenyl.

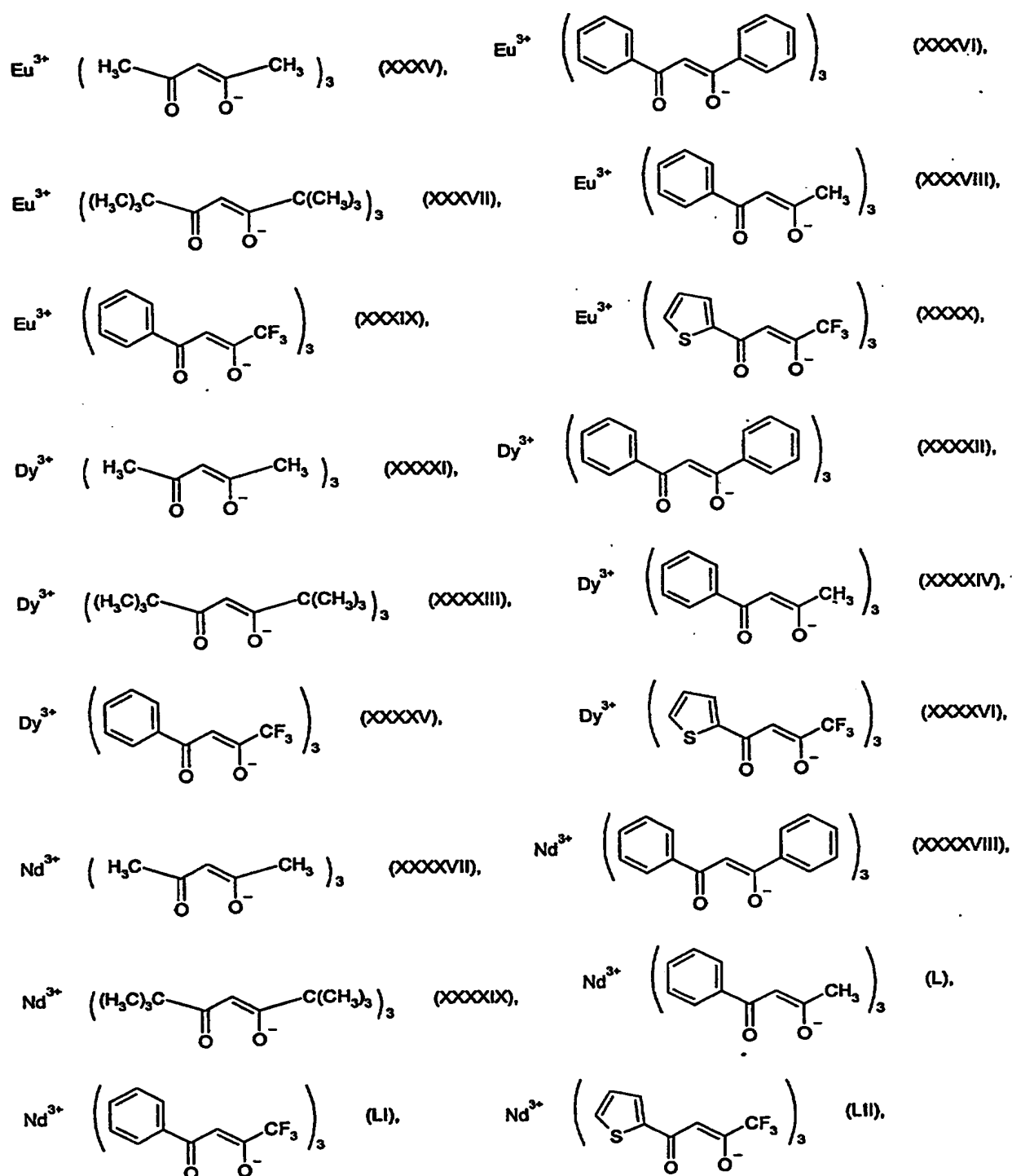
R<sub>2</sub> in formula II is preferably hydrogen.

Particularly preferred as component (a) are the compounds of formula XIII to CVI:

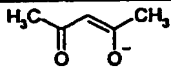
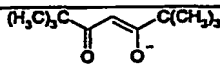
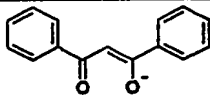
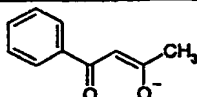
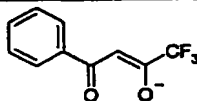
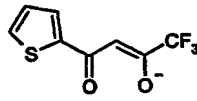








Some preferred derivatives of structures of type II and III, derived from the above drawn preferred structures of type I, are compiled in the table below:

L	DMAP	DMAP	DMAP	DMAP	DMAP	Et <sub>3</sub> NH <sup>+</sup>	Et <sub>3</sub> NH <sup>+</sup>	Et <sub>3</sub> NH <sup>+</sup>	Et <sub>3</sub> NH <sup>+</sup>	Et <sub>3</sub> NH <sup>+</sup>
Ln	Tb	Eu	Sm	Dy	Nd	Tb	Eu	Sm	Dy	Nd
Ch <sup>-</sup>										
	LIII	XVIII	LXII	LXVIII	LXXIII	LXXIX	LXXXIV	LXXXIX	LXXXXV	CI
	XV	LVIII	LXIII	XVI	LXXIV	XXII	LXXXV	LXXXX	LXXXXVI	CII
	LIV	XVII	LXIV	LXIX	LXXV	LXXX	XXI	LXXXI	LXXXXVII	CIII
	LV	LIX	LXV	LXX	LXXVI	LXXXI	LXXXVI	LXXXII	LXXXXVIII	CIV
	LVI	LX	LXVI	LXXI	LXXVII	LXXXII	LXXXVII	LXXXIII	LXXXXIX	CV
	LVII	LXI	LXVII	LXXII	LXXVIII	LXXXIII	LXXXVIII	LXXXIV	C	CVI

DMAP: 4-dimethylaminopyridine

Further suitable lanthanide chelates may contain

- pyridine, aminopyridine, pyrrolidinopyridine, methylpyridine, methoxypyridine, pyridine-N-oxide, bipyridine, phenanthroline, imidazole or any other derived or similar N, O or S containing mono- or polydentate ligand in place of DMAP

piperidinium, ammonium, alkylammonium, dialkylammonium, trialkylammonium, pyridinium or any other similar N containing protonated species in place of Et<sub>3</sub>NH<sup>+</sup>

For certain applications it is recommendable to use a combination of different lanthanides, for example Eu and Tb. Such a mixture increases the degree of security of the hidden colourations, the sophistication of the security level and multiplies the coding possibilities.

The compounds of formula I, II, III and IV are known, for instance from WO 96/20942 and from C.R. Hurt et al., *Nature* **212**, 179-180 (1966), or can be prepared by methods known per se. For example, a ligand such as acetylacetone, benzoylacetone, dibenzoylmethane,

dipivaloylmethane, salicylic acid, valeric acid or caproic acid can be reacted under suitable conditions with a rare earth metal halide such as a lanthanide trichloride to produce the rare earth metal chelate. Further reaction with the monodentate or polydentate nitrogen-, oxygen- or sulfur-containing ligand L thus yielding the rare earth metal chelate compounds of formula I, II, III and IV.

The luminescent lanthanide chelate can be applied as a powder, as a solution or as a dispersion.

Accordingly, component (b) may be water, an organic solvent, a mixture of two or more organic solvents or a mixture of water and one or more organic solvents.

Preferably, component (b) is water, one or more water-miscible organic solvents or a mixture of water and one or more water-miscible organic solvents.

Suitable organic solvents include alcohols, glycols, ether alcohols, sulfoxides, amides, amines, heterocyclic solvents, ketones, ethers, esters, nitriles and aliphatic, cycloaliphatic and aromatic hydrocarbons.

Examples of suitable organic solvents are methanol, ethanol, n-propanol, isopropanol, n-butanol, glycerol, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, ethylene glycol monoethylether, polyethyleneglycol dimethylether, ethoxybutanol, 2-butoxyethanol, dimethylsulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMA), N-methylpyrrolidone (NMP), acetone, 2-butanone, diethylether, di-n-propylether, tetrahydrofurane (THF), ethyl acetate, ethyl propionate, acetonitrile, pyridine, n-pentane, n-hexane, cyclohexane, benzene and toluene.

The water-miscible organic solvent is preferably an aliphatic alcohol, etheralcohol, glycol, aliphatic ketone, carboxylic acid ester, carboxylic acid amide, aliphatic nitrile, aliphatic polyether or aliphatic sulfoxide.

Particularly preferred water-miscible organic solvents are ethanol, 2-butoxyethanol, ethylene glycol, propylene glycol, acetone, 2-butanone, ethyl acetate, tetrahydrofurane (THF), dimethylformamide (DMF), dimethylacetamide (DMA), N-methylpyrrolidone (NMP), acetonitrile, polyethyleneglycol dimethylether and dimethylsulfoxide (DMSO).

The compositions according to the invention may, in addition to components (a) and (b), comprise one or more colorants (c).

Suitable colorants are the well-known pigments and dyes including mixtures of different pigments and dyes.

In the compositions according to the present invention the amounts of components (a) and (b) and where appropriate (c) and/or further ingredients (d) can vary within wide ranges.

For a mass-dyeing process, the compositions according to the present invention consist of component (a). Optionally, further ingredients (c) and/or (d) may also be added together with (a) in order to give simultaneous supplementary property(ies) to the polymeric material in addition to the UV-luminescence.

For a dyeing process, preferred compositions contain 0.01 to 20.0 %, more preferably 0.05 to 10 % and in particular 0.1 to 5.0 %, by weight of component (a) and 80.0 to 99.99 %, more preferably 90.0 to 99.95 % and in particular 95.0 to 99.9 %, by weight of component (b), based on the total amount of components (a) + (b).

The amount of component (c) depends on the type of substrate as well as on the specific pigment or dye. Advantageous amounts will generally be 0.01% to 15% by weight and especially 0.1% to 10% by weight, of colorant based on the weight of fibre.

Further ingredients (d) which may be present in the compositions according to the invention are e.g. optical brighteners, biocides, bactericides, fungicides insecticides and fragrance.

The compositions containing at least one lanthanide chelate can be prepared by any suitable method known to those of ordinary skill in the art. For example, the components of the composition can be combined and mixed in a suitable mixer or blender.

The compositions according to the invention are useful for impregnating manufactured natural, artificial and especially synthetic hydrophobic materials, especially textile materials.

Textile materials composed of blend fabrics comprising such manufactured natural polymer or synthetic hydrophobic fiber materials can likewise be impregnated with the formulations of the invention.

Useful manufactured natural polymer textile materials are especially wool, cotton, silk, cellulose acetate and cellulose triacetate.

Synthetic hydrophobic textile materials are especially linear aromatic polyesters, for example polyesters formed from a terephthalic acid and glycols, particularly ethylene glycol, or condensation products of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane; polycarbonates, for example those formed from  $\alpha,\alpha$ -dimethyl-4,4'-dihydroxydiphenylmethane and phosgene; or fibres based on polyvinyl chloride or polyamide.

The formulations according to the invention are applied to the textile materials according to known dyeing processes. For example, polyester fibres are exhaust dyed from an aqueous dispersion in the presence of customary anionic or nonionic dispersants with or without customary carriers at temperatures between 80 and 140°C, preferably between 120 and 135°C. Cellulose acetate is preferably dyed at between 60 to 85°C and cellulose triacetate at up to 115°C.

The formulations used according to the invention are useful for dyeing by the thermosol, exhaust and continuous processes and for printing processes. The exhaust process is preferred. The liquor ratio depends on the apparatus, the substrate and the make-up form. However, the liquor ratio can be chosen to be within a wide range, for example in the range from 4:1 to 100:1, but it preferably is between 6:1 to 25:1.

The textile material mentioned may be present in the various processing forms, for example as a fibre, yarn or web or as a woven or loop-formingly knitted fabric.

The luminescent lanthanide chelates of the invention are likewise useful for mass-dyeing of plastics.

Accordingly, the invention further relates to a process for the preparation of luminescent plastics characterized in that the plastics material is extruded in the presence of 0.01 – 10.0

% by weight, based on the amount of plastics material, of a compound of formula I, II, III or IV.

Plastics useful for mass dyeing include for example dyeable high molecular weight organic materials (polymers) having a dielectric constant  $\geq 2.5$ , especially polyester, polycarbonate (PC), polystyrene (PS), polypropylene (PP), polymethyl methacrylate (PMMA), polyamide, polyethylene, polypropylene, styrene/acrylonitrile (SAN) or acrylonitrile/butadiene/styrene (ABS). Preference is given to polyester and polyamide. Particular preference is given to linear aromatic polyesters obtainable by polycondensation of terephthalic acid and glycols, especially ethylene glycol, or condensation products of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane, for example polyethylene terephthalate (PET) or polybutylene terephthalate (PBTP); polycarbonates, for example polycarbonates formed from  $\alpha,\alpha$ -dimethyl-4,4'-dihydroxydiphenylmethane and phosgene; polymers based on polyvinyl chloride or polyamide, for example nylon 6 or nylon 6.6, polystyrene (PS) or polypropylene (PP).

Very particular preference is given to plastics based on linear aromatic polyesters, for example those formed from terephthalic acid and glycols, particularly ethylene glycol, or condensation products of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane, polymethyl methacrylate (PMMA), polypropylene (PP) or polystyrene (PS).

The plastics are dyed for example by mixing the luminescent lanthanide chelate according to component (a) into these substrates using roll mills or mixing or grinding apparatus whereby the lanthanide chelates are dissolved or finely dispersed in the plastic. The plastic with the admixed dyes is then processed in a conventional manner, for example by calendering, pressing, extrusion, spread coating, spinning, casting or injection moulding, whereby the dyed material acquires its ultimate shape. The mixing of the components can also be effected directly prior to the actual processing step, for example by continuously metering solid, for example pulverulent, lanthanide chelates and a granulated or pulverulent plastic and also optionally additional substances such as for example additives simultaneously directly into the inlet zone of an extruder where the mixing-in takes place just prior to the processing. In general, however, prior mixing of the lanthanide chelates into the plastic is preferable, since more uniformly impregnated substrates are obtainable.

The invention further relates to luminescent textile fibre and to luminescent plastic prepared by the process described above.

The present invention makes it possible to incorporate colourless or coloured hidden marks into various colourless, white, pale coloured or dark coloured substrates, which can be revealed under UV exposure.

The claimed process is particularly useful for the manufacture of security fibres or security threads that can be applied to fiduciary documents or other materials.

Security fibres are incorporated in fiduciary documents or other materials for the purpose of ensuring identification, an authentication, a protection against forgery, imitation or falsification. Security threads are continuous threads or strips of film introduced into fiduciary documents for the same purpose as security fibres.

The expression "fiduciary documents" denotes papers, such as papers for bank notes, cheques, shares, bills, stamps, official documents, identity cards, passports, record books, notes, tickets, vouchers, bulletins, accounting books as well as credit, payment, access or multifunctional cards, and similar documents which necessarily involve a high degree of security.

The manufacture of security fibres or security threads can be accomplished by known methods as described, for example, in U.S. Patents Nos. 4,655,788, 5,759,349 and 6,045,656, EP-A 185 396 and EP-A 1 013 824.

Incorporation of the lanthanide chelate compound can be carried out by conventional dyeing or printing processes.

Suitable fibres for the claimed process can be obtained from wood or vegetable pulp, cellulose pulp, cotton, linen or synthetic fibres.

Preferably, paper fibres or synthetic fibres are used.

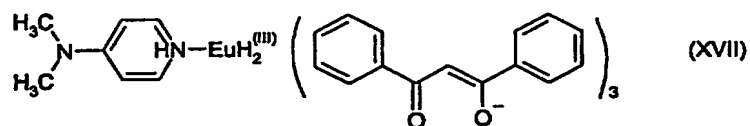
In a particularly preferred embodiment the process according to claim 1 is used for the preparation of anti-counterfeit documents, cards, cheques or banknotes.

The compositions according to the invention distinguish from analogous prior art compositions by outstanding luminescence quantum yield, long-lasting luminescence and high luminescence intensity.

The following Examples illustrate the invention.

Ink Composition A:

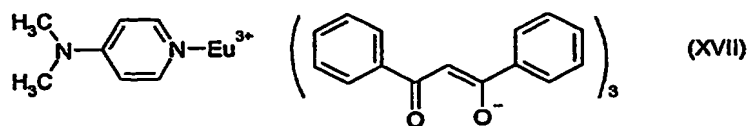
Concentrate of compound XVII in 1,2-propylene glycol



1 g of compound VIII is dissolved in 99 g of 1,2-propyleneglycol under heating at 100°C for 1 hour. The clear yellow solution is allowed to cool down and after filtration (clarification) provides the stable Ink Composition A which exhibits an intense red luminescence under UV light. This concentrate can be further used in either solvent based or aqueous based conventional or high-tech (ink-jet) printing formulations for paper, textile, leather, wood, plastic or other compatible substrates.

Example 1:

The impregnation of a cellulosic bobbin (0.75kg cotton thread 40tex) is performed at 35°C for 20 min in an alternated circulation dyeing apparatus (Callebault de Blicquy) (3 min cycle) with a liquor ratio of 1 to 10. The liquor contains 4.5% of the compound of formula XVII



in 2-butoxy-ethanol.

After treatment, centrifugation and air-drying of the bobbin, strong red-orange fluorescence is observed under UV light.



**Example 2:**

The impregnation of a silk thread (10g) is performed at 25°C for 10-60 min in the same liquor and liquor ratio to textile material as described in Example 1. After treatment, centrifugation and air-drying of the thread reveals strong red-orange fluorescence under UV light.

**Example 3:**

The impregnation of a patchwork fabric containing several distinct bands of synthetic, artificial, natural (vegetal and animal) fibers (20g) is performed at 25°C for 10-60 min in the same liquor and liquor ratio to textile material as described in Example 1. After treatment, centrifugation and air-drying of the patchwork reveals on most fibers strong red-orange fluorescence under UV light.

Equivalent results are obtained from similar processes using other lanthanide complexes, exhibiting other emission wavelength under irradiation in the UV (e.g. terbium, dysprosium, samarium, neodymium).

**Example 4:**

*High temperature dyeing (HTD) of a polyester (PES) filament (135°C, 60min)*

A PES filament (10g) is introduced in a 250mL bottle tight against leakage, containing 200ml of dyeing bath (i.e. bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- a solvent-based solution (5 to 30ml) containing 3-5% of the lanthanide complex of formula XVII dissolved in NMP
- an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogencarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated PES filament exhibits a strong red-orange fluorescence under irradiation at 365nm.

**Example 5:**

**High temperature dyeing (HTD) of a velvet PES fabric (135°C, 60min)**

A velvet PES fabric (10g) is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (i.e. bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- o a solvent-based solution (5 to 30mL) containing 3-5% of the lanthanide complex of formula XVII dissolved in NMP
- o an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogenocarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated PES filament exhibits a strong red-orange fluorescence under irradiation at 365nm.

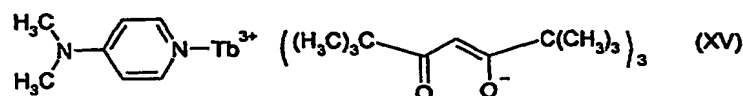
**Example 6:**

**High temperature dyeing (HTD) of a velvet PES fabric (135°C, 60min)**

A white velvet PES fabric (10g) is introduced in a 250mL bottle tight against leakage, containing 200ml of dyeing bath (i.e. bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- o a solvent-based solution (5 to 30ml) containing 3-5% of the lanthanide complex XV



dissolved in NMP

- o an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogenocarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated velvet PES fabric is white and exhibits a strong green fluorescence under irradiation at 254nm.

**Example 7:**

***High temperature dyeing (HTD) of a polyamide (PA) tricot (135°C, 60min)***

A PA tricot (10g) is introduced in a 250mL bottle tight against leakage, containing 200mL of dyeing bath (*i.e.* bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- a solvent-based solution (5 to 30mL) containing 3-5% of the lanthanide complex XVII dissolved in NMP
- an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogencarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated PA tricot exhibits a strong red-orange fluorescence under irradiation at 365nm.

**Example 8:**

***High temperature dyeing (HTD) of a PA tricot (135°C, 60min)***

A white PA tricot (10g) is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (*i.e.* bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- a solvent-based solution (5 to 30mL) containing 3-5% of the lanthanide complex XV dissolved in NMP
- an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)

- 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
- 0.4g/l sodium hydrogenocarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated PA tricot is white and exhibits a green fluorescence under irradiation at 254nm.

**Example 9:**

*High temperature dyeing (HTD) of a transparent colourless PA thread (135°C, 60min)*

A transparent colourless PA thread (10g) is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (i.e. bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- a solvent-based solution (5 to 30ml) containing 3-5% of the lanthanide complex XVII dissolved in NMP
- an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogenocarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated transparent PES thread exhibits a strong red-orange fluorescence under irradiation at 365nm.

**Example 10:**

*Incorporation of XVII in polyamide (PA) by mass-dyeing process*

Extruded Ultramid B3K in the presence of 2% of the lanthanide complex XII for 2 min at 260°C results in red-orange fluorescence upon irradiation at 365nm.

**Example 11:**

*Incorporation of XVII in polystyrene (PS) by mass-dyeing process*

Extruded Polystyrol H165 in the presence of 2% of the lanthanide complex XVII for 5 min at 300°C results in red-orange fluorescence upon irradiation at 365nm.

**Example 12:**

***Incorporation of XVII in polypropylene (PP) by mass-dyeing process***

A homogenised mixture of polypropylene granules (200g) and compound XVII (2g) is introduced in the fusion chamber (200°C) of a 3mm cable extruder. After cooling in a water bath, the thus obtained rigid cable is cut into granules again, which are in turn introduced in the fusion chamber (230°C) of a filament extruder. The thus obtained transparent multifilament thin polypropylene thread (8dtex) exhibits a strong red-orange fluorescence upon excitation at 365nm.

**Example 13:**

***Incorporation of XVII in polypropylene (PP) by mass-dyeing process***

Similar process and resulting fluorescent properties are obtained with simultaneous use of Titanium dioxide together with compound XVII.

**Example 14:**

***Incorporation of XVII in poly(methylmethacrylate) (PMMA) by mass-dyeing process***

Extruded Plexiglas 6N in the presence of 2% of the lanthanide complex XVII for 5 min at 260°C results in red-orange fluorescence upon irradiation at 365nm.

**Example 15:**

***Incorporation of XVII in acrylonitrile/butadiene/styrene-copolymer (ABS) by mass-dyeing process***

Extruded Terluran 877M in the presence of 2% of the lanthanide complex XVII for 5 min at 220°C results in red-orange fluorescence upon irradiation at 365nm.

**Example 16:**

***High temperature dyeing (HTD) of a coloured PES thin thread (135°C, 60min)***

A thin cyan PES thread (10g) - previously mass-dyed with a mixture of Irgalite Blue GLGP (C.I. Pigment Blue 15:3), titanium dioxide (C.I. Pigment White 6) and carbon black (C.I. Pigment Black 7) - is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (i.e. bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions:

- a solvent-based solution (5 to 30ml) containing 3-5% of the lanthanide complex XV dissolved in NMP
- an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogencarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated thin cyan PES thread is cyan and exhibits a strong green fluorescence under irradiation at 254nm and no fluorescence under irradiation at 365nm.

**Example 17:**

*High temperature dyeing (HTD) of a coloured PES thin thread (135°C, 60min)*

A thin black PES thread (10g) - previously mass-dyed with a pigment mixture containing titanium dioxide (*C.I. Pigment White 6*) and carbon black (*C.I. Pigment Black 7*) - is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (*i.e.* bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions:

- a solvent-based solution (5 to 30ml) containing 3-5% of the lanthanide complex XV dissolved in NMP
- an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogenocarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated thin black PES thread is

black and exhibits a strong green fluorescence under irradiation at 254nm and no fluorescence under irradiation at 365nm.

**Example 18:**

*High temperature dyeing (HTD) of a coloured PES thin thread (135°C, 60min)*

A thin yellow PES thread (10g) - previously mass-dyed with Filester Yellow RNB(C.I.

*Pigment Yellow 147*) - is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (i.e. bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions:

- a solvent-based solution (5 to 30ml) containing 3-5% of the lanthanide complex XV dissolved in NMP
- an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogencarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated thin yellow PES thread is yellow and exhibits a strong green-yellow fluorescence under irradiation at 254nm and no fluorescence under irradiation at 365nm.

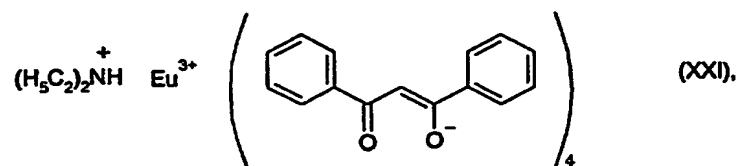
**Example 19:**

*High temperature dyeing (HTD) of a PES filament (135°C, 60min)*

A PES filament (10g) is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (i.e. bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- a solvent-based solution (5 to 30ml) containing 3-5% of the lanthanide complex



dissolved in NMP

- an aqueous solution at pH=4.5 (195 to 170mL) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogenocarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated PES filament exhibits a strong red-orange fluorescence under irradiation at 365nm.

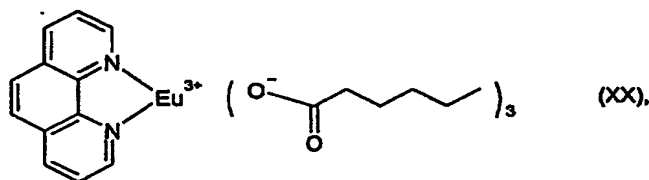
#### Example 20:

##### *High temperature dyeing (HTD) of a PES filament (135°C, 60min)*

A white PES filament (10g) is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (*i.e.* bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- a NMP suspension (5 to 30ml) containing 2% of the lanthanide complex



- an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogenocarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C),



spin dried and finally dried with hot air (90-105°C). The thus treated white PES filament is white and exhibits a pink-red fluorescence under irradiation at 254nm and no fluorescence under irradiation at 365nm.

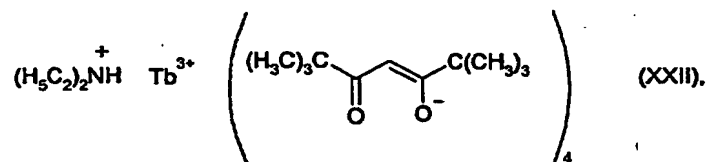
**Example 21:**

**High temperature dyeing (HTD) of a PES filament (135°C, 60min)**

A white PES filament (10g) is introduced in a 250ml bottle tight against leakage, containing 200ml of dyeing bath (i.e. bath ratio 1 to 20).

The dyeing bath is prepared as a mixture of the following two solutions :

- o a solvent-based solution (5 to 30ml) containing 3-5% of the lanthanide complex



dissolved in NMP

- o an aqueous solution at pH=4.5 (195 to 170ml) containing
  - 0.6g/l of Univadin DP (Ciba Specialty Chemicals)
  - 2.5g/l of Cibatex AB 45 (Ciba Specialty Chemicals)
  - 0.4g/l sodium hydrogenocarbonate

The bottle is installed in a rotating high temperature dyeing autoclave with a starting bath temperature of 70°C. The temperature is then raised to 135°C over 30 min and kept stable for further 1 hour. The treatment temperature is finally decreased down to 40°C over 15 min, after which the thread is removed from the bottle, rinsed for 5 min with warm water (35°C), spin dried and finally dried with hot air (90-105°C). The thus treated white PES filament is white and exhibits a green fluorescence under irradiation at 254nm and no fluorescence under irradiation at 365nm.

**Example 22:**

**High temperature dyeing (HTD) of PES (135°C, 60min)**

All above experiments of High Temperature Dyeing are also realised without using NMP, by a similar preparation method to that of Disperse Dyes, and by replacing the Disperse Dye with the UV fluorescent lanthanide chelate to be applied.

**Example 23:**

Transfer printing with UV fluorescent lanthanide chelates is performed by using transfer printing formulations containing one or more UV fluorescent lanthanide chelates. These formulations are prepared in a similar way to conventional transfer printing formulations, either by using one or more lanthanide chelates in place of disperse dyes, or by using one or more lanthanide chelates in addition to the disperse dye(s).

**Example 24:**

***Preparation of a multi-component security thread***

A polymer mixture (e.g. copolymerised polyamide Akulon®, supplied by Akzoplastiks) is distributed to three extruders and the granules are melted. The melts indicated for the outer components of the thread are each mixed with 3 % by weight of a compound of formula (XVII) in such a way that it dissolves homogeneously in the polyamide melt. After extrusion of the multi-component threads a security thread is obtained the edge strips of which fluoresce under UV light whereas the central strip does not show any fluorescence. Co-extrusion of the lanthanide chelate(s) with one or more dyes or pigments provides coloured threads which are similarly fluorescent under UV light.

**Example 25:**

***Preparation of a multi-component security thread***

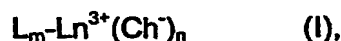
As described in Example 24, a security thread is prepared by extrusion of a polyamide melt containing 3 % by weight of a 1:1 mixture of a compound of formula (XVII) and a compound of formula (XV). Upon irradiation of UV light of different wavelengths red and/or green fluorescence is observed.

What is claimed is

1. A process for the preparation of luminescent polymeric fibres characterised in that the fibres are treated with a composition comprising

- (a) one or more luminescent lanthanide chelates containing three or four organic anionic ligands having at least one UV absorbing group and
- (b) one or more solvents.

2. A process according to claim 1 characterized in that component (a) is a compound of formula I



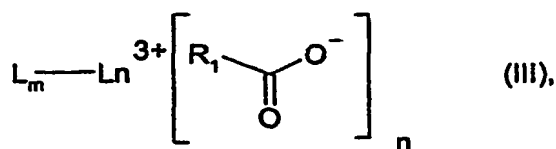
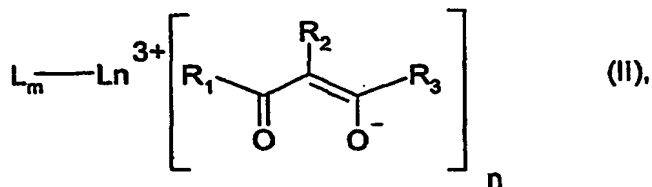
wherein Ln represents a lanthanide,

Ch<sup>-</sup> is a negatively charged ligand containing at least one UV absorbing double bond,

n denotes 3 or 4, m denotes a number from 0 to 4,

in case n is 3, m denotes a number from 0 to 4 and L is a neutral monodentate or polydentate nitrogen-, oxygen- or sulfur-containing ligand or, in case n is 4, m denotes 1 and L is a single-charged cation.

3. A process according to claim 1 characterized in that component (a) is a compound of formula II, III or IV



wherein Ln represents a lanthanide,

n denotes 3 or 4, m denotes a number from 0 to 4

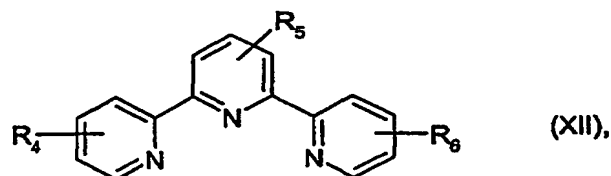
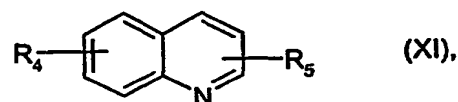
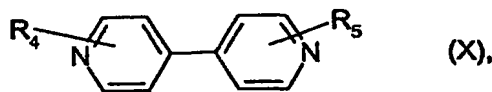
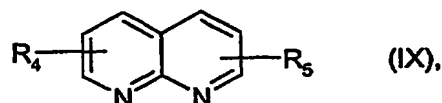
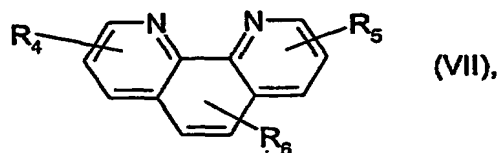
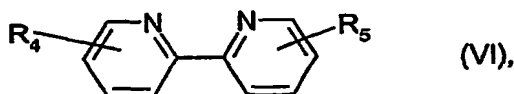
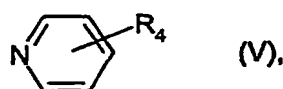
in case n is 3, m denotes a number from 0 to 4 and L is a neutral monodentate or polydentate nitrogen-, oxygen- or sulfur-containing ligand or, in case n is 4, m denotes 1 and L is a single-charged cation,

$R_2$ , is hydrogen or  $C_1$ - $C_6$ alkyl, and

$R_1$  and  $R_3$  are each independently of the other hydrogen,  $C_1$ - $C_6$ alkyl,  $CF_3$ ,  $C_5$ - $C_{24}$ aryl or  $C_4$ - $C_{24}$ heteroaryl.

4. A process according to claim 2 or 3 characterized in that component (a) is a compound of formula I, II, III or IV wherein n denotes 3 and L is a nitrogen-containing ligand.

5. A process according to claim 2 or 3 characterized in that component (a) is a compound of formula I, II, III or IV wherein L is a compound of formulae V to XII



or a cation of the formula  $H-N^+(R_7)_3$ ,

wherein  $R_4$ ,  $R_5$  and  $R_6$  are each independently of the other hydrogen, halogen,  $C_1$ - $C_6$ alkyl,  $C_5$ - $C_{24}$ aryl,  $C_6$ - $C_{24}$ aralkyl,  $C_1$ - $C_6$ alkoxy, amino, dialkylamino or a cyclic amino group and  $R_7$  is hydrogen,  $C_1$ - $C_6$ alkyl,  $C_5$ - $C_{24}$ aryl,  $C_6$ - $C_{24}$ aralkyl or vinyl.

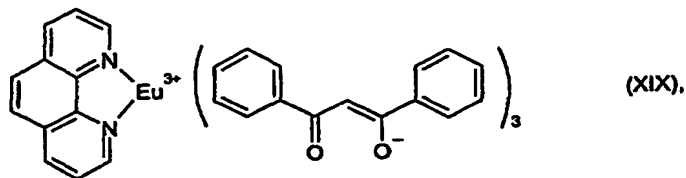
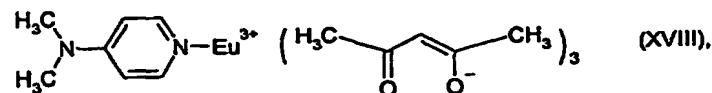
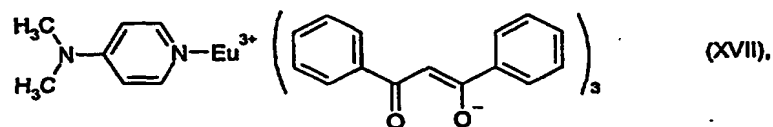
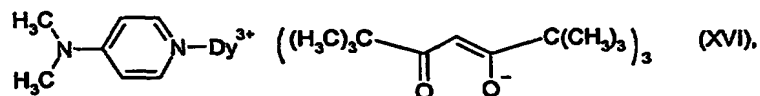
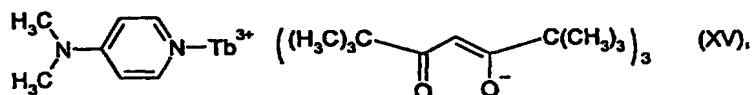
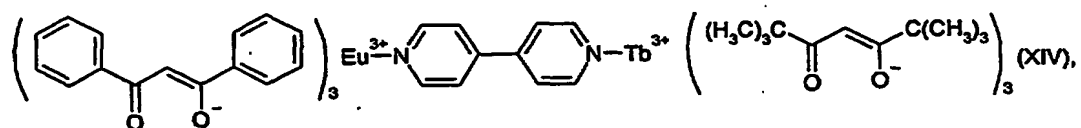
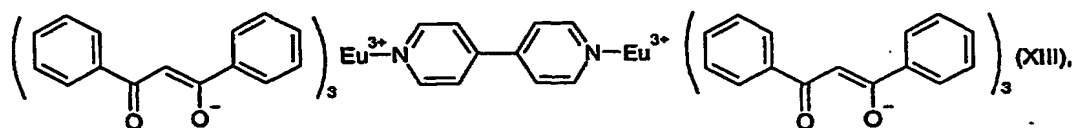
6. A process according to claim 5 characterized in that component (a) is a compound of formula II wherein L is a compound of formula V, VI, VII, VIII, IX, X, XI or XII wherein  $R_4$ ,  $R_5$  and  $R_6$  are hydrogen, methyl, amino, pyrrolidino or dimethylamino or L is a cation of the formula  $H-N^+(R_7)_3$  wherein  $R_7$  is  $C_1$ - $C_6$ alkyl.

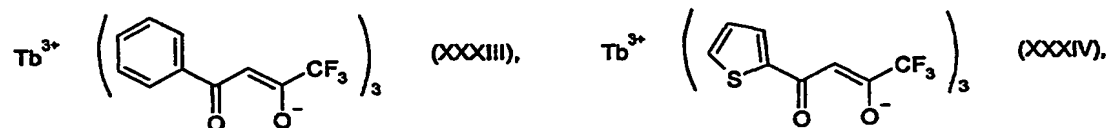
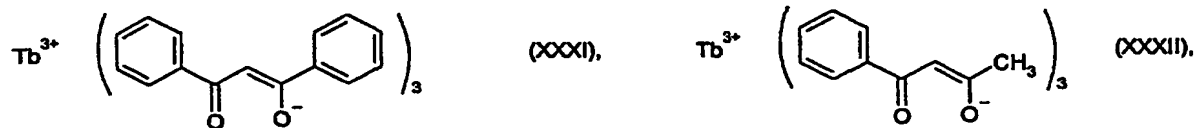
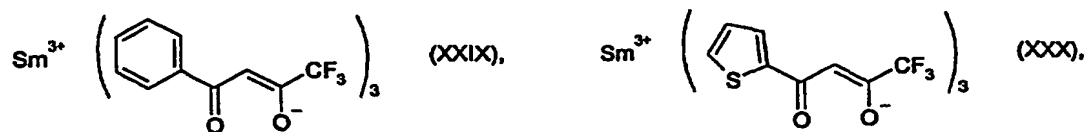
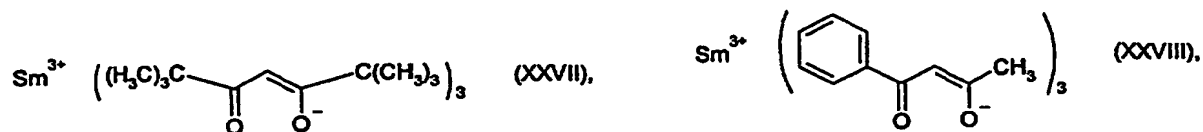
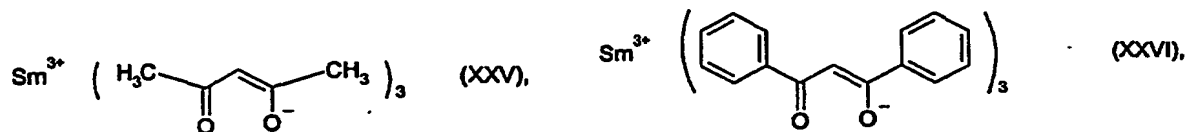
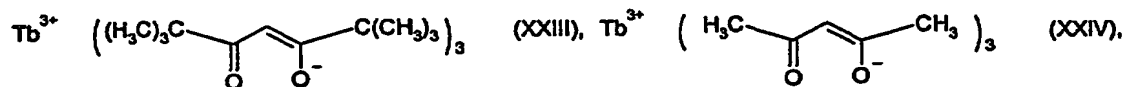
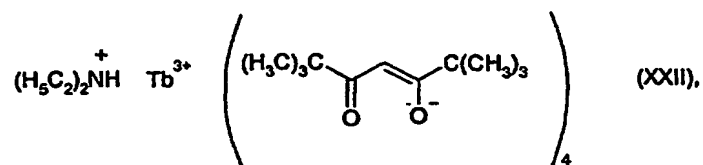
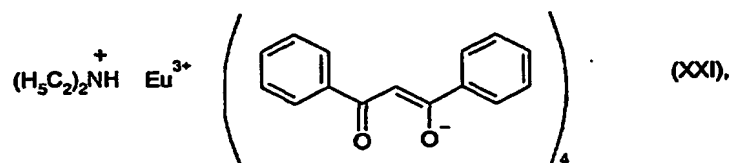
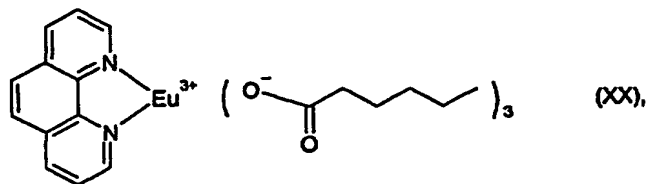
7. A process according to claim 2 or 3 characterized in that component (a) is a compound of formula I, II, III or IV wherein Ln is Eu, Tb, Dy, Sm or Nd.

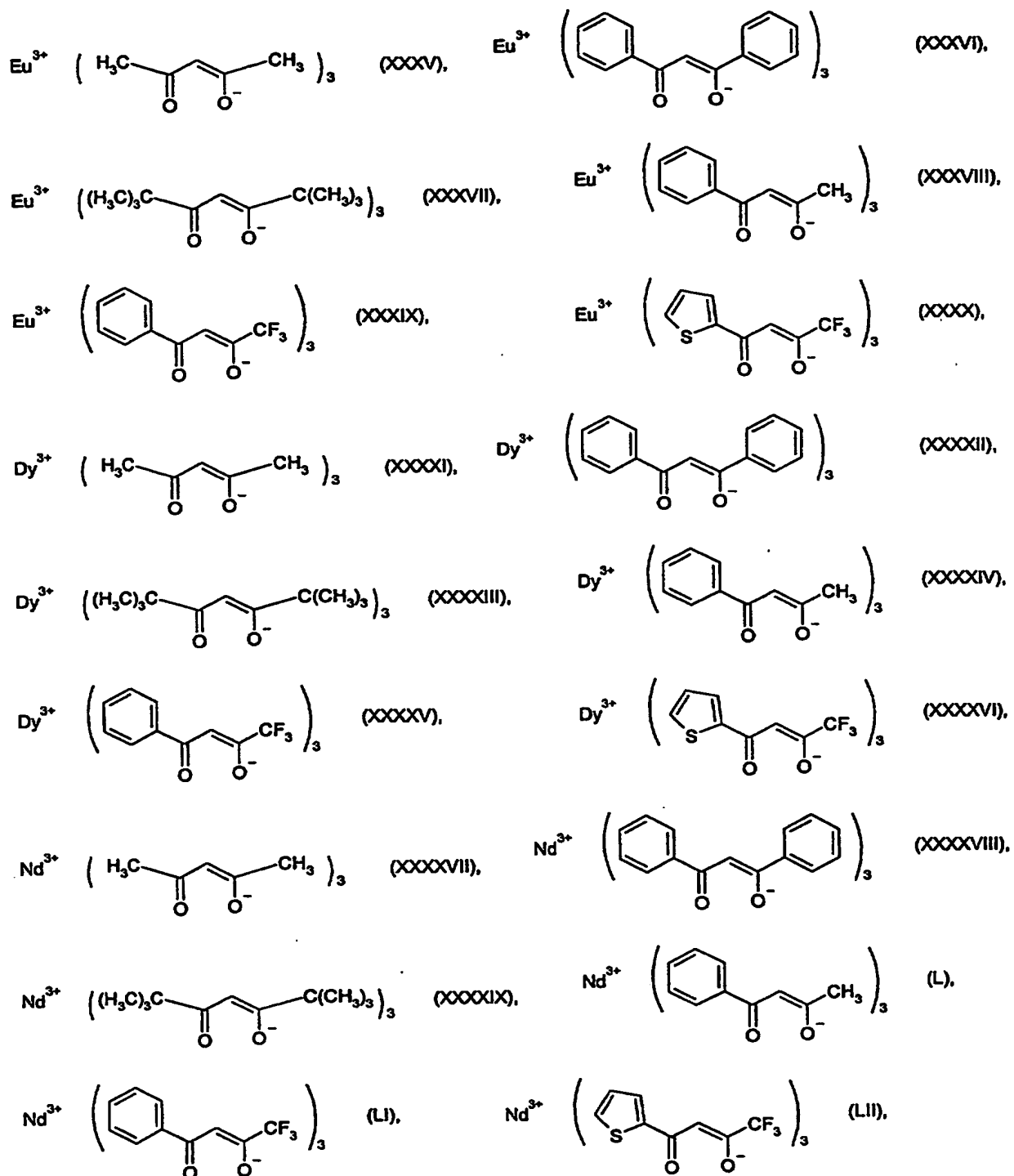
8. A process according to claim 3 characterized in that component (a) is a compound of formula II or III wherein R<sub>1</sub> and R<sub>3</sub> are methyl, t-butyl, n-pentyl or phenyl.

9. A process according to claim 3 characterized in that component (a) is a compound of formula II wherein R<sub>2</sub> is hydrogen.

10. A process according to claim 3 characterized in that component (a) is a compound of formula XIII to LII







11. A process according to claim 1 or 2 characterized in that component (b) is water, one or more water-miscible organic solvents or a mixture of water and one or more water-miscible organic solvents.

12. A process according to claim 11 characterized in that the water-miscible organic solvent is an aliphatic alcohol, etheralcohol, glycol, aliphatic ketone, carboxylic acid ester, carboxylic acid amide, aliphatic nitrile, aliphatic polyether or aliphatic sulfoxide.

13. A process according to claim 11 characterized in that the water-miscible organic solvent is selected from the group consisting of ethanol, 2-butoxyethanol, ethylene glycol, propylene glycol, acetone, 2-butanone, ethyl acetate, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylacetamide (DMA), N-methylpyrrolidone (NMP), acetonitrile, polyethyleneglycol dimethylether and dimethylsulfoxide (DMSO).

14. A process according to claim 1 characterized in that the formulation contains 0.01 to 20.0 % by weight of component (a) and 80.0 to 99.99 % by weight of component (b), based on the total amount of components (a) + (b).

15. A process according to claim 1 characterized in that the formulation contains additionally (c) one or more colorants.

16. A process for the preparation of luminescent plastics characterized in that the plastics material is extruded in the presence of 0.01 – 10.0 % by weight, based on the amount of polymeric material, of a compound of formula II or III according to claim 3.

17. A luminescent textile fibre prepared by the process according to claim 1.

18. A luminescent plastic prepared by the process according to claim 16.

19. A process according to claim 1 wherein the polymeric fibres are paper fibres or synthetic fibres.

20. The use of the process according to claim 1 for the preparation of anti-counterfeit documents, cards, cheques or banknotes.



**Ink Compositions**

**Abstract**

The invention relates to a process for the preparation of luminescent textile fibres characterized in that the fibres are treated with a composition comprising

- (a) one or more luminescent lanthanide chelates containing three organic anionic ligands having at least one UV absorbing group and
- (b) one or more solvents.

PCT Application  
PCT/EP2003/011638

